RP245

INTERFERENCE MEASUREMENTS IN THE FIRST SPECTRA OF KRYPTON AND XENON

By C. J. Humphreys

ABSTRACT

The wave lengths of the stronger arc lines of krypton and xenon have been redetermined by the use of Febry-Perot étalon interferometers. Étalons of 15, 25, and 40 mm length were used in obtaining the data. Discharge tubes operated so as to emit only the spectrum of the neutral atom of the gas under investigation supplied the radiation. Part of the xenon lines were observed as impurity lines in the radiation from krypton-filled tubes as well as in tubes containing pure xenon only. The secondary standards of neon photographed simultaneously with the Kr or Xe spectrum furnished the comparison. The values of neon wave lengths used were those given by Burns.

Interferometer measurements of a sufficient number of krypton lines have been made to permit fixing the relative values of all the $1s$, $2p$, and $3p$ terms to a high degree of precision. The accuracy of the term values is such that the average deviation of calculated term combinations from the observed wave numbers is 1 part in 20,000,000. The corresponding set of terms in the xenon spectrum, except $2p_{10}$, were determined also with increased precision from interference measurements. In addition to these, four of the $4p$ terms have been recalculated. Nearly three-fourths of the combinations permitted by the selection rule have been observed. The exact location of the combinations in the infra-red region not photographically accessible can now be predicted with certainty. Such lines should prove useful wave-length standards for the infra-red region.

With the resolving power employed none of the krypton lines showed hyperfine structure. It is apparent from the extremely small variations of the "constant differences" that the intensities of any unobserved satellites are too low to affect the wave lengths. Five of the xenon lines showed satellites. Further work is contemplated in the examination of the lines of both spectra for hyperfine structure.

The results here presented are compared with earlier interferometer measurements. The close agreement of our results with those of other observers as well as the small differences between our separate observations indicate that the wave lengths of the radiation emitted by krypton or xenon are reproducible within the limits set by the probable error of the observations. For the intense green and yellow lines of krypton, for which Perard, at the International Bureau obtained wave lengths 5,570.2892 and 5,870.9154 A, we obtain 5,570.2890 and 5,870.9153 A.

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I. INTRODUCTION

The work here reported represents another step in a complete investigation of the spectra of krypton and xenon which has been undertaken in this laboratory. An historical account of earlier work on these gases, a discussion of the reasons for the present investigation, and a preliminary description, together with an interpretation of

the first spectra of krypton and xenon, are contained in two earlier papers by Meggers, deBruin, and Humphreys.[1] The wave lengths of the stronger arc lines have now been redetermined by comparison with the secondary standards of neon, using the method of Fabry-Perot étalon interferometers.[2] The new wave-length data have led to increased precision in the relative values of the lowest terms, and to an accurate prediction of the location of infra-red lines inaccessible to photography. The investigation of certain lines as possible substitutes for the Cd primary standard will require an examination of these lines for hyperfine structure by aid of an interferometer of higher resolving power than has been used in the work to date. Such an investigation is to be undertaken in the near future.

II. EXPERIMENTAL PROCEDURE

The sources of radiation were glass tubes of the same type used in the earlier work on Kr and Xe.[3] The krypton tubes contained a small amount of xenon as an impurity, and in new tubes the stronger xenon lines appeared together with the krypton spectrum. The xenon wave lengths were determined from spectrograms obtained with tubes containing pure xenon and from Xe impurity lines measured in the krypton spectrograms. A similar tube filled with neon furnished the comparison spectrum; the values of the wave lengths were those obtained by Burns, Meggers, and Merrill[4] from comparison with the primary standard. The choice of neon instead of cadmium was prompted by ease of use, the accuracy with which its wave lengths have been determined, the intensity of the radiation, the sharpness of the interference patterns, and the fact that there are several lines in the vicinity of the primary standard. In general, the optical distance between the interferometer plates can be determined more accurately from several lines than from a single one, and if the Ne lines are chosen so that the average wave length is nearly the same as that of the primary standard, the wave lengths to be measured, as well as the corrections due to dispersion of phase and to atmospheric conditions, are all referred to the same point in the spectrum as if the primary standard had been used. The use of such a group of lines is essentially equivalent to the use of the primary standard itself; it has the sanction of the International Astronomical Union.[5] Six or more lines chosen for comparison were selected from among the following, the choice usually depending on the observed intensities: 6,266.4950, 6,304.7893, 6,334.4280, 6,382.9913, 6,402.2455, 6,506.5278, 6,532.8827, 6,598.9528, and 6,678.2760 A.

The Ne comparison source was always photographed simultaneously with the radiation from the Kr or Xe gas. This served to eliminate systematic errors which might arise from a displacement of any portion of the apparatus due to thermal effects or mechanical disturbances. The light from the comparison source was thrown into the path of the direct beam by aid of a piece of clear plate glass set at an angle of 45° in the line joining spectrograph and source,

[1] Meggers, deBruin, Humphreys, B. S. Jour. Research, **3**, pp. 129 and 731; 1929.
[2] Fabry and Buisson, J. de Phys., **7**, p. 169; 1908; also Astrophys. J., **28**, p. 169; 1908.
[3] Meggers, deBruin, Humphreys, B. S. Jour. Research, **3**, pp. 129 and 731; 1929.
[4] Burns, Meggers, and Merrill, B. S. Sci. Papers (S329), **14**, p. 765; 1918. Burns, J. Opt. Soc. Am., **11**, p. 301; 1925.
[5] Trans. I. A. U., **2**, p. 40; 1925.

permitting the direct beam to be transmitted with little loss. Because of the high intensity of the neon red lines the amount of radiation reflected was sufficient to produce a strong comparison spectrum.

The tubes have been operated with a "G. E. sign transformer," by connecting the Ne and Kr or Xe tubes in series to the secondary. The transformer is rated to give 12,000 volts and draws a maximum primary current of 2.7 amp at 110 volts. To avoid overheating the tubes the primary current was reduced to about 1.6 amp by introducing resistance into the primary circuit.

The spectrograph employed was a Hilger E2, fitted with glass optical parts in order that the dispersion in the red and infra-red region might be sufficient to separate the numerous lines occurring in this part of the spectrum.

The interferometer plates were of glass, 40 mm in diameter, but with the aperture restricted to 28 mm by the central opening in the separators. The plates were lightly silvered by the method of cathodic deposition. When the silvered surfaces were held so as to form a thin wedge, 12 images of a 40-watt lamp could be seen through them. Reflecting power was deliberately sacrificed for transparency, so that the effective wave lengths of as many lines as possible could be determined with reasonable exposures. The resolving power was not sufficient to detect hyperfine structure in the krypton lines, but it clearly indicated such structure for certain xenon lines, viz, 4,500, 4,734, 8,231, 8,409, and 8,819 A. Invar separators of 2, 3, 15, 25, and 40 mm length were employed. The reasons for the use of several étalons will be discussed in connection with the evaluation and correction of wave lengths.

The mountings for the étalons were of the same design as those originally employed by Fabry and Perot, and illustrated by a cut in one of their early publications.[6] Light from the source fell upon the interferometer plates after being converted into a parallel beam by a short-focus lens. The ring system was projected upon the spectograph slit by means of an achromatic lens. A quartz-fluorite lens of about 25 cm focal length was used in connection with the smaller separators and a glass achromatic lens, taken from a large Hilger interferometer, of 50 cm focal length with the larger separators. The use of the projector of greater focal length is required with the longer étalons because of the relatively smaller angular diameters of the rings in the interference pattern with increasing orders of interference (retardations). The source, lenses, and interferometer were all accurately lined up in coincidence with the optic axis of the spectrograph.

The plates were sensitized with a mixed dye bath, containing pinaverdol, pinacyanol, dicyanin, rubrocyanin, and neocyanin. This procedure was necessary in order to cover the entire range of wave lengths, including the region occupied by neon, in single exposures. The exposure times ranged from 5 minutes to 3 hours. One exposure of 12 hours, taken for the purpose of recording the interference pattern of the Xe line at 9,799.65 A, failed to show the line with intensity sufficient for measurement, although a trace could be seen. An hourly record of the temperature in the vicinity of the interferometer was kept. The variation over the entire exposure period was usually from 0.1° to 0.2° C. In only one exposure did it amount to 0.6° C.

[6] Fabry and Perot, Astrophys. J., 15, p. 73; 1902.

III. DETERMINATION OF WAVE LENGTHS AND TERM VALUES

1. REDUCTION OF DATA

The theory of the Fabry-Perot interferometer, and the methods used in the reduction of observations have been treated very fully by Fabry and Buisson,[7] and many other observers. We shall confine ourselves to a brief development of the essential formulas and discussion of their application, referring the reader to the original papers for a more detailed account.

The retardation suffered by a beam of light, which has been reflected twice at the parallel surfaces of an air film of thickness e, is given by $P=\frac{2e\cos i}{\lambda}$, where i is the angle of incidence and λ the wave length. The retardation will be increased by the same amount for each successive pair of reflections. The value of i equal to zero or normal incidence corresponds to the center of a system of circular fringes, since points in the field of view corresponding to equal values of i lie upon a circle. The order or retardation at the center, designated by p becomes, therefore, $p=\frac{2e}{\lambda}$. The angle of incidence may be expressed by $\frac{\alpha}{2}$ where α is the angular diameter of a ring. It is equal to the angle subtended at the optical center of the projecting lens by the diameter of the ring which is imaged upon the slit of the spectrograph, and may be expressed as the product of the diameter of the corresponding ring on the photographic negative and a magnification factor. By substitution we obtain for any order $P=p\cos\frac{\alpha}{2}$. Since α is a small angle, the order at the center may be expressed to a sufficiently close approximation by $p=P+P\frac{\alpha^2}{8}$. The retardation P corresponding to a bright ring must be a whole number. For each successive ring proceeding outward the value of P is diminished by 1. The order, p, at the center is equal to the sum of the integral order, P_1, of the first ring and a fraction $P_1\frac{\alpha^2}{8}$, which we shall call ϵ.

The length of the étalon is a constant. Consequently, if a standard wave length is known, and if one can determine the retardation experimentally for any radiation, one can compare the standard wave length with any other. This follows at once from the equation

$$2e=\lambda p=\lambda' p'= \ldots\ldots$$

The problem of comparison of wave lengths is reduced, therefore, to the determination of the exact order of interference at the center of the ring system corresponding to each radiation.

The fractional part of the retardation may be computed from the diameters of two or more successive rings, by a method described by Childs.[8] The form in which it is given here is due to Burns and Kiess.[9] As indicated above, the order at the center of the ring

[7] Fabry and Buisson, Astrophys. J., 28, p. 169; 1908.
[8] Childs, J. Sci. Inst., 3, pp. 97 and 129; 1926.
[9] Burns and Kiess, Pub. Allegheny Obs., 6, p. 125; 1927.

system is given in terms of the angular diameter of a ring as $p=P_n+P_n\frac{a^2}{8}$. In terms of ring diameters this may be written $p=P_n+FD_n^2$. Since the whole orders of successive rings differ by unity the retardation may be expressed in terms of the order of any ring and the difference in retardation between the first ring and the center of the system;

$$p=P_1+\epsilon=P_2+1+\epsilon=P_3+2+\epsilon=\ldots\ldots$$

Consequently

$$\epsilon=FD_1^2$$

$$1+\epsilon=FD_2^2$$

$$2+\epsilon=FD_3^2, \text{ etc.}$$

We have finally:

$$\epsilon=\frac{D_1^2}{D_2^2-D_1^2}=\frac{D_2^2}{D_3^2-D_2^2}-1=\frac{D_3^2}{D_4^2-D_3^2}-2=\ldots\ldots$$

A check on the accuracy of the measurements is given by the fact that the differences of squares of successive ring diameters are constant for a given wave length and change progressively with wavelength. Whenever possible we have measured at least four ring diameters, thus obtaining three values of ϵ of which the average was taken. This is the first step in the reduction.

The next step is the determination of $2e$ for the étalon used. The method described by Meggers [10] which has already been mentioned, making use of several Ne lines was employed. The method presupposes a knowledge of the approximate étalon length and very accurate values of the standard wave lengths. When the correct whole order has been found for any one line, $2e$ is determined closely enough so that there is satisfactory agreement between the observed and computed fractional orders for each of the standard lines. The value of $2e$ adopted was the mean of the products, λp, for the set of standards used.

The evaluation of the Kr or Xe wave lengths followed in two steps. The quotient of $2e$ divided by the approximate wave length indicated the integral part of the retardation. This was then combined with the correctly determined fractional part and divided into $2e$, yielding the more precise wave length. The corrections made necessary by variation of the index of refraction of the air from the value at 15° C. and 760 mm pressure were calculated and applied to the individual sets of measurements, using the results of the investigation by Meggers and Peters.[11] The corrections for dispersion of phase due to apparent unequal penetration of the reflecting films by different waves were calculated from preliminary values of wave lengths obtained from thick and thin étalons as illustrated by Meggers.[12] The measurements obtained from small étalons, 2 and 3 mm were used for this purpose and to give preliminary values of the wave lengths. Since any given

[10] Meggers, B. S. Sci. Papers (S251), 12, p. 203; 1915.
[11] Meggers and Peters, B. S. Sci. Papers (S327), 14, p. 697; 1918.
[12] Meggers, B. S. Sci Papers (S251), 12, p. 199; 1915.

wave length is not, in general, known with sufficient precision to give the integral order of interference without ambiguity in the case of large retardations arising from long étalons, it is advisable to work with a series of étalons of increasing lengths. These lengths should not form integral ratios. With such a series of observations any error due to wrong whole order is immediately obvious. The precision attainable is roughly proportional to the retardation and hence to the étalon thickness, the accuracy of ring measurements being about the same in all cases. It is the common experience of workers in this field that results obtained from small orders of interference show rather poor agreement. Since we have found this to be the case in the present investigation, the corrected values obtained from the 15, 25, and 40 mm. étalons only have been assembled to compute the final set of wave lengths. The krypton wave lengths were calculated from measurements of 13 spectrograms, which were obtained from krypton filled tubes containing sufficient xenon as an impurity to give most of its spectrum also. Six spectrograms were measured which were obtained with tubes giving a pure xenon spectrum. The wave lengths of xenon have thus been assembled from the results of 19 individual observations. On account of considerable range in intensity, the weak lines appearing only with long exposures, and the strong lines being in some cases too heavily overexposed for measurement, not all lines were observed on all plates.

Estimates of intensity and sharpness of the interference pattern were recorded and these, together with the order of interference, were taken into account in weighting individual values to give the final result. The method of determining the final set of wave lengths was first to compute a weighted mean of the values given for one étalon and apply the phase corrections to these values, after which a mean of means was obtained for the results from the three different étalons weighted according to the order of interference. The wave lengths were reduced to the values of vacuum by the Cauchy dispersion formula as given in the paper by Meggers and Peters.[13]

2. EXPERIMENTAL RESULTS AND DISCUSSION

The final values of the wave lengths, together with wave numbers and term combinations are given in Tables 1 and 2. In the case of Xe lines showing hyperfine structure only the wave length of the main component is given here, since these appear in every case to give the same level separations as the simple lines. The tables of Kr and Xe lines form systems of spectroscopic standards comparable in accuracy of relative values to those determined earlier for Ne and A.

The new wave-length data have permitted the redetermination of the $1s$, $2p$, and $3p$ terms in the case of krypton. Table 3 shows these terms and their combinations arranged in a supermultiplet. The value of the $1s_5$ term is that previously found from series calculations. Differences between calculated and observed term values are indicated where interferometer measurements are available. Grating measurements followed by calculated values in parentheses are given for lines observed with the grating only. Calculated values of unobserved but permitted combinations are also given in parentheses.

[13] Meggers and Peters, B. S. Sci. Papers (S327), 14, p. 627; 1918.

Of the 60 permitted combinations, 35 are obtained from interferometer measurements, 15 are observed by the grating only, and 10 are unobserved, 7 of which lie in the infra-red region inaccessible to photography. The xenon terms and combinations are assembled in a similar manner in Table 4, giving $1s_5$ the value obtained from series. We have sufficient interferometer data to redetermine the $1s$, $2p$, and $3p$ terms, except $2p_{10}$ which involves the line 9,799.65 A. It will be recalled that there are only six $3p$ terms. In addition, we have data permitting the recalculation of four of the $4p$ terms. Of the 57 permitted combinations between these terms, 32 are obtained from interferometer measurements, 14 are observed with the grating only, and 11 are unobserved, 8 of which lie in the region beyond 9,200 A.

TABLE 1.—*Krypton I, interference measurements*

λ, air	λ, vac.	ν cm⁻¹	Combination
8, 928. 6934	8, 931. 1420	11, 196. 7764	$1s_5-2p_{10}$
8, 776. 7498	8, 779. 1572	11, 390. 6150	$1s_4-2p_8$
8, 508. 8736	8, 511. 2085	11, 749. 2128	$1s_2-2p_4$
8, 298. 1091	8, 300. 3869	12, 047. 6312	$1s_4-2p_7$
8, 263. 2412	8, 265. 5096	12, 098. 4676	$1s_2-2p_2$
8, 190. 0570	8, 192. 3056	12, 206. 5759	$1s_4-2p_6$
8, 112. 9023	8, 115. 1300	12, 322. 6615	$1s_5-2p_9$; $2p_9-4d_4$
8, 104. 3660	8, 106. 5914	12, 335. 6408	$1s_5-2p_8$
8, 059. 5053	8, 061. 7186	12, 404. 3030	$1s_3-2p_4$
7, 928. 602	7, 930. 780	12, 609. 100	$2p_8-4d_4$
7, 913. 443	7, 915. 617	12, 633. 254	$2p_{10}-4d_5$
7, 854. 823	7, 856. 981	12, 727. 535	$1s_3-2p_3$
7, 746. 831	7, 748. 960	12, 904. 958	819. 90
7, 694. 5401	7, 696. 6547	12, 992. 6577	$1s_5-2p_7$
7, 685. 2472	7, 687. 3593	13, 008. 3682	$1s_2-2p_1$
7, 601. 5465	7, 603. 6360	13, 151. 6027	$1s_5-2p^6$
7, 587. 4135	7, 589. 4992	13, 176. 0999	$1s_4-2p_5$
7, 486. 850	7, 488. 908	13, 353. 082	$2p_{10}-4d_6$; $2p_9-3s$
7, 287. 262	7, 289. 267	13, 718. 801	$2p_{10}-2s_2$
7, 224. 109	7, 226. 097	13, 838. 729	$2p_{10}-4d_3$
6, 456. 293	6, 458. 074	15, 484. 493	$2p_{10}-5d'_4$
6, 421. 028	6, 422. 799	15, 569. 536	$2p_8-5d_4$
6, 012. 111	6, 013. 772	16, 628. 499	$2p_{10}-5d_3$; $2p_6-5s$
5, 993. 8500	5, 995. 5063	16, 679. 1585	$1s_4-2p_4$
5, 870. 9153	5, 872. 5386	17, 028. 4108	$1s_4-2p_2$
5, 649. 5627	5, 651. 1267	17, 695. 5863	$1s_3-3p_{10}$
5, 570. 2890	5, 571. 8318	17, 947. 4190	$1s_5-2p_3$
5, 562. 2251	5, 563. 7658	17, 973. 4381	$1s_5-2p_2$
4, 812. 607	4, 813. 948	20, 772. 971	$1s_3-4X$
4, 550. 298	4, 551. 569	21, 970. 446	$1s_4-3p_{10}$
4, 502. 3546	4, 503. 6133	22, 204. 3931	$1s_4-3p_8$
4, 463. 6897	4, 464. 9382	22, 396. 7266	$1s_4-3p_7$
4, 453. 9183	4, 455. 1642	22, 445. 8618	$1s_4-3p_6$
4, 425. 1909	4, 426. 4293	22, 591. 5728	$1s_2-3p_4$
4, 418. 769	4, 420. 006	22, 624. 404	$1s_2-5Y$
4, 410. 369	4, 411. 603	22, 667. 498	$1s_2-3p_3$
4, 399. 9675	4, 401. 1992	22, 721. 0802	$1s_2-3p_2$
4, 376. 1217	4, 377. 3471	22, 844. 8870	$1s_4-3p_5$
4, 362. 6429	4, 363. 8648	22, 915. 4670	$1s_5-3p_{10}$
4, 351. 3605	4, 352. 5794	22, 974. 8824	$1s_2-3p_1$
4, 319. 5798	4, 320. 7904	23, 143. 9137	$1s_5-3p_1$
4, 318. 5523	4, 319. 7626	23, 149. 4203	$1s_5-3p_8$
4, 300. 4877	4, 301. 6932	23, 246. 6602	$1s_3-3p_4$
4, 286. 4875	4, 287. 6894	23, 322. 5849	$1s_3-3p_3$
4, 282. 9686	4, 284. 1695	23, 341. 7469	$1s_5-3p_7$
4, 273. 9705	4, 275. 1691	23, 390. 8876	$1s_5-3p_6$

TABLE 2.—*Xenon I, interference measurements*

λ. air	λ. vac.	ν cm⁻¹	Combination
9, 162. 654	9, 165. 166	10, 910. 877	$1s_4-2p_7$
9, 045. 446	9, 047. 926	11, 052. 256	$1s_5-2p_9$
8, 952. 254	8, 954. 709	11, 167. 309	$\begin{cases}1s_4-2p_6\\1s_3-3p_9\end{cases}$
8, 819. 412	8, 821. 831	11, 335. 515	$1s_5-2p_8$
8, 409. 190	8, 411. 498	11, 888. 489	$1s_5-2p_7$
8, 346. 823	8, 349. 114	11, 977. 318	$1s_2-2p_3$
8, 280. 1163	8, 282. 3893	12, 073. 811	$1s_4-2p_5$
8, 231. 6348	8, 233. 8947	12, 144. 921	$1s_5-2p_6$
7, 967. 341	7, 969. 529	12, 547. 792	$1s_3-3p_7$
7, 887. 3898	7, 889. 5565	12, 674. 984	$1s_2-2p_1$
7, 642. 026	7, 644. 126	13, 081. 940	$\begin{cases}1s_3-2p_2\\3d_4-5V\end{cases}$
7, 584. 680	7, 586. 765	13, 180. 849	$3d'_4-5Z$
7, 393. 791	7, 395. 824	13, 521. 143	$2p_6-5d_1''$
7, 386. 002	7, 388. 033	13, 535. 401	$2p_{10}-3s_5$
7, 285. 298	7, 287. 302	13, 722. 500	$2p_7-4d_2$
7, 119. 598	7, 121. 557	14, 041. 872	$\begin{cases}2p_7-2s_3\\2p_8-5d'_4\end{cases}$
6, 882. 1543	6, 884. 0496	14, 526. 333	$2p_9-5d_4$
6, 827. 315	6, 829. 195	14, 643. 014	$1s_3-4X$
6, 318. 062	6, 319. 805	15, 823. 272	$2p_8-6d'_4$
5, 028. 2785	5, 029. 6767	19, 881. 994	$1s_4-3p_{10}$
4, 923. 1522	4, 924. 5224	20, 306. 538	$1s_4-3p_9$
4, 916. 508	4, 917. 876	20, 333. 981	$1s_4-2p_4$
4, 843. 294	4, 844. 643	20, 641. 357	$1s_4-3p_6$
4, 829, 709	4, 831. 054	20, 699. 415	$1s_4-3p_7$
4, 807. 019	4, 808. 358	20, 797. 118	$1s_4-3p_5$
4, 792. 6192	4, 793. 9547	20, 859. 605	$1s_5-3p_{10}$
4, 734. 1524	4, 735. 4724	21, 117. 217	$1s_4-2p_3$
4, 697. 020	4, 698. 330	21, 284. 155	$1s_5-3p_9$
4, 690. 9711	4, 692. 2797	21, 311. 603	$1s_5-2p_4$
4, 671. 226	4, 672. 529	21, 401. 685	$1s_5-3p_8$
4, 624. 2757	4, 625. 5666	21, 618. 973	$1s_5-3p_6$
4, 611. 8896	4, 613. 1773	21, 677. 034	$1s_5-3p_7$
4, 582. 7474	4, 584. 0274	21, 814. 878	$1s_4-2p_1$
4, 524. 6805	4, 525. 4451	22, 094. 833	$1s_5-2p_3$
4, 500. 9772	4, 502. 2356	22, 211. 188	$1s_5-2p_2$
4, 385. 7693	4, 386. 9973	22, 794. 635	$1s_4-4X$
4, 383. 9092	4, 385. 1367	22, 804. 306	$1s_4-4Y$
4, 203. 6945	4, 204. 8746	23, 781. 922	$1s_5-4Y$
4, 193. 5296	4, 194. 7071	23, 839. 567	$1s_5-4U$
4, 135. 123	4, 136. 285	24, 176. 285	$1s_4-4p_9$
4, 116. 1151	4, 117. 2723	24, 287. 925	$1s_4-4p_7$
4, 109. 7093	4, 110. 8648	24, 325. 782	$1s_4-4p_6$
4, 078. 8207	4, 079. 9681	24, 509. 996	$1s_4-4p_5$
3, 967. 541	3, 968. 659	25, 197. 423	$1s_5-4p_8$
3, 950. 925	3, 952. 039	25, 303. 391	$1s_5-4p_6$

TABLE 3.—*Krypton I, sp combinations*

		$1s_2$ $j=1$ 27,068.497	655.089	$1s_3$ 0 27,723.586	4,274.858	$1s_4$ 1 31,998.444	945.026	$1s_5$ 2 32,943.470
$3p_1$ j=0	4,093.615	22,974.882 0		*		(27,904.829)		*
$3p_2$ 2	4,347.417	22,721.080 0		*		27,651.061 (1.027)		28,596.37 (6.053)
$3p_3$ 1	4,401.000	22,667.498 −1	655.087	23,322.585 +1		(27,597.444)		28,542.65 (2.470)
$3p_4$ 1	4,476.925	22,591.573 −1	655.087	23,246.660 +1		27,521.66 (1.519)		28,466.83 (6.545)
$3p_5$ 0	9,153.557	17,915.21 (4.940)		*		22,844.887 0		*
$3p_6$ 2	9,552.582	17,516.05 (5.915)		*		22,445.862 0	945.026	23,390.888 0
$3p_7$ 1	9,601.720	17,466.99 (6.777)		18,122.22 (1.866)		22,396.727 −3	945.020	23,341.747 +3
$3p_8$ 2	9,794.050	17,274.94 (4.447)		*		22,204.393 +1	945.027	23,149.420 0
$3p_9$ 3	9,799.556	*		*		*		23,143.914 0
$3p_{10}$ 1	10,028.000	17,040.50 (0.497)		17,695.586 0	4,274.860	21,970.446 −2	945.021	22,915.467 +3
$2p_1$ 0	14,060.129	13,008.368 0		*		(17,938.315)		*
$2p_2$ 2	14,970.032	12,098.468 −3		*		17,028.411 +1	945.027	17,973.438 0
$2p_3$ 1	14,996.051	12,072.36 (2.446)		12,727.535 0		17,002.45 (2.393)		17,947.419 0
$2p_4$ 1	15,319.284	11,749.213 0	655.090	12,404.303 −1	4,274.856	16,679.159 +1		17,624.34 (4.186)
$2p_5$ 0	18,822.344	(8,246.153)		*		13,176.100 0		*
$2p_6$ 2	19,791.868	(7,276.629)		*		12,206.576 0	945.027	13,151.603 −1
$2p_7$ 1	19,950.812	(7,117.685)		(7,772.774)		12,047.631 +1	945.027	12,992.658 0
$2p_8$ 2	20,607.829	(6,460.668)		*		11,390.615 0	945.026	12,335.641 0
$2p_9$ 3	20,620.808	*		*		*		12,322.662 0
$2p_{10}$ 1	21,746.694	(5,321.803)		(5,976.892)		11,251.75 (1.750)		11,196.776 0

TABLE 4.—*Xenon I, sp combinations*

		$1s_2$ $j=1$ 20,649.467	988.208	$1s_3$ 0 21,637.735	8,151.629	$1s_4$ 1 29,789.364	977.616	$1s_5$ 2 30,766.980
$4p_5$ $j=0$	5,279.368	15,370.54 (0.099)		*		24,509.996 0		*
$4p_6$ 2	5,463.585	15,186.11 (5.882)		*		24,325.782 −3	977.609	25,303.391 +4
$4p_7$ 1	5,501.439	(15,147.028)		(16,136.296)		24,287.925 0		25,265.31 (5.541)
$4p_8$ 3	5,569.557	*		*		*		25,197.423 0
$3p_5$ 0	8,992.246	11,657.21 (7.221)		*		20,797.118 0		*
$3p_6$ 2	9,148.007	11,501.57 (1.460)		*		20,641.358 −1	977.615	21,618.973 0
$3p_7$ 1	9,089.948	11,559.51 (9.519)		12,547.791 −4		20,699.415 +1	977.619	21,677.034 −2
$3p_8$ 3	9,365.295	*		*		*		21,401.685 0
$3p_9$ 2	9,482.826	(11,166.641)		*		20,306.538 0	977.617	21,284.155 −1
$3p_{10}$ 1	9,907.374	10,742.17 (2.093)		11,730.44 (0.361)		19,881.994 −4	977.611	20,859.605 +1
$2p_1$ 0	7,974.486	12,674.984 −3		*		21,814.878 0		*
$2p_2$ 1	8,555.793	12,093.65 (3.674)		13,081.940 +2		21,233.66 (3.571)		22,211.188 −1
$2p_3$ 2	8,672.147	11,977.318 +2		*		21,117.217 0	977.616	22,094.833 0
$2p_4$ 1	9,455.380	11,194.03 (4.087)		12,182.36 (2.355)		20,333.981 +3	977.621	21,311.602 −2
$2p_5$ 0	17,715.553	(2,933.914)		*		12,073.811 0		*
$2p_6$ 2	18,622.057	(2,027.410)		*		11,167.309 −2	977.612	12,144.921 +3
$2p_7$ 1	18,878.489	(1,770.978)		(2,759.246)		10,910.877 −2	977.612	11,888.489 +2
$2p_8$ 3	19,431.465	*		*		*		11,335.515 0
$2p_9$ 2	19,714.724	(934.743)		*		10,074.74 (4.640)		11,052.256 0
$2p_{10}$ 1	20,565.33	(84.14)		(1,072.40)		(9,224.03)		10,201.65

An idea of the relative accuracy of the wave lengths can be obtained best from the internal agreement shown by the terms. As indicated in Table 3, the residuals, obtained by subtracting observed from computed term values, average less than 1 part in 20,000,000 in the case of krypton. Wave lengths have been carried out to four places of decimals for all lines for which the probable error of the weighted mean does not exceed 0.0005 A. The wave lengths of xenon are considered slightly inferior to those of krypton, partly because several of the lines showed hyperfine structure, and partly, because the spectrum was out of range for good observation at the extremes. The ultra-violet lines are relatively weak, being higher term combinations, and the last three measured lines in the infra-red are hard to obtain without overexposing the rest of the plate. The remarkably close agreement of the "constant differences" between wave numbers both in the Kr and Xe spectra furnish additional examples of the precision with which the Ritz combination principle can be verified. It is not likely that any other physical law can be checked more precisely. Another valuable result is the accurate prediction of wave lengths in the infra-red region. These should prove useful standards for use in connection with bolometric observations.

3. COMPARISON OF THE WORK OF OTHER OBSERVERS

Attention is called to a number of earlier investigations which have been made with interferometers to determine the wave lengths of some of the stronger lines of krypton and xenon. Fabry and Buisson [14] first compared the bright green and yellow lines of krypton with the primary Cd standard (6,438.4696 A) and obtained wave lengths 5,570.2908 and 5,870.9172 A, respectively. Meggers [15] determined the wave lengths of 17 krypton lines (4,273.9696 to 7,601.544 A) and 12 xenon lines (4,500.978 to 4,923.152 A) also using the primary standard for comparison. His values for the green and yellow Kr lines were 5,570.2872 and 5,870.9137 A. A comparison of his values for kyrpton with those of the present investigation, for the purpose of detecting any systematic differences, indicates that the new values are 0.0008 A, higher on the average, if the measurements of the weak line at 6,456 A, for which no great precision is claimed, is retained. Omission of this line reduces the difference to 0.0006 A. Only five of the wave lengths in Meggers' list are given to the fourth decimal place. It is apparent, therefore, that this difference of the order of 1 part in 10,000,000 is no greater than could be accounted for by the probable error of the observations. The agreement of the xenon wave lengths is even better. The wave lengths given in the present paper are 0.0003 A lower on the average if the measurements of the line at 4,829 A, for which there is a difference of 0.004 A between two sets of measurements, is retained. Omission of this line makes the average of the present measurements 0.0001 A higher than the earlier. This difference amounts to 1 part in 50,000,000, far less than the probable error claimed for the observations. The tubes used by Meggers were operated at very low pressures on account of the small quantity of

[14] Fabry and Buisson, Comptes Rendus, 156, p. 945; 1913.
[15] Meggers, B. S. Sci. Papers (S411), 17, p. 193; 1921.

gas available. The results indicate the reproducibility of the wave lengths under different conditions, including a considerable range in pressure.

The measurements of the green and yellow lines were repeated by Perard,[16] who obtained 5,570.2892 and 5,870.9154 A for their values using the Cd standard for comparison. These wave lengths are nearly a mean of those given by Buisson and Fabry, and those given by Meggers. Our latest results for the same lines check those of Perard very closely, being 5,570.2890 and 5,870.9153. Weber[17] measured three lines of Kr (5,649.5924, 5,870.9463, and 6,456.3241) relative to Cd (6,438.5033 A in air at 20° C. 760 mm Hg and 10 mm water vapor) and proposed the yellow-green line (5,649.5924 A.) as a primary standard to replace the red line of Cd.

In a recent paper by McLennan and Quinlan[18] it is claimed that xenon lines are unsuitable as standards on account of a pressure shift toward shorter wave lengths appearing as the tubes become aged. The results of four exposures are presented, all made with the same tube and with one étalon of 5 mm length. For the first observation 2 infra-red wave lengths are given; for the second, 1; for the third, 8; and for the fourth, 12. The one line (8,231.635 A) which appears in all four exposures we have found to have at least three hyperfine structure components, which makes the unresolved pattern obtained with small étalons difficult to measure accurately. As pointed out above, the measurements of wave lengths obtained with small étalons and consequent low orders of interference always show larger errors than similar results obtained with higher retardations.

To disprove the so-called pressure effect announced by McLennan and Quinlan, Tables 5 and 6 are presented to show the manner in which our individual measurements agree. A selection from among the measured spectrograms has been made to compare successive exposures on the same plate, to present results obtained with different tubes, and different étalons and to ascertain if there was any effect due to aging of tubes. We consider first Table 5, containing Kr data. Observations numbered 5*c* and 5*b* were made with a 15 mm étalon on the same plate with the same tube. No time elapsed between the two exposures, save the few seconds required to rack down the plate. This tube had been used in several earlier exposures and no record of its age was kept. The other spectrograms 10*a*, 10*b*, 12*a*, 12*b* were made with a newer tube. It had been used five hours before making exposure 10*a* in addition to some running time while the apparatus was being adjusted. A short exposure of about an hour intervened between those numbered 10 and 12. The dates of the exposures are indicated. It is quite apparent that the variations between exposures on the same plate are of the same order as those obtained with different tubes or the same tube at a later date. We have no reason to believe that the small variations which occur have any other explanation than the probable error of individual observations.

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[16] Perard, Comptes Rendus, **176**, p. 1060; 1923.
[17] Weber, Physik. Zeit., **29**, p. 233; 1928.
[18] McLennan and Quinlan, Trans. Roy. Soc. Canada, **24**, Sec. III, p. 1; 1930.

TABLE 5.—*Comparison of corrected krypton wave lengths*

5*c* 15 mm March 5 3 hours	5*b* 15 mm March 5 1 hour	12*a* 25 mm March 12 2 hours	12*b* 25 mm March 12 24 min.	10*a* 40 mm March 10 1 hour	10*b* 40 mm March 10 3 hours
8,928.6952	8,928.6941			8,928,6919	8,928.6941
8,776.7519	8,776.7479	8,776.7480		8,776.7456	8,776.7532
8,508.8767	8,508.8717	8,508.8701		8,508.8705	8,508.8719
8,298.1144	8,298.1114	8,298.1104	8,298.1045	8,298.1082	
8,263.2414	8,263.2404	8,263.2416	8,263.2427	8,263.2393	
8,190.0562	8,190.0552	8,190.0564	8,190.0542	8,190.0580	8,190.0580
8,112.9081	8,112.9051	8,112.9050	8,112.9005	8,112.9014	8,112.9019
8,104,3651	8,104,3611	8,104.3673	8,104.3616	8,104.3640	8,104,3709
8,059.5061	8,059.5051	8,059.5060		8,059.5030	8,059.5056
7,854.8258	7,854.8209	7,854.8248	7,854.8235	7,854.8227	7,854.8244
7,746.8347					7,746.8295
7,694.5456	7,694.5406	7,694.5446	7,694.5392	7,694.5390	7,694.5384
7,685.2426	7,685.2516	7,685.2481	7,685.2503	7,685.2476	7,685.2517
7,601.5525	7,601.5475	7,601.5488	7,601.5453	7,601.5455	
7,587.4145	7,587.4055	7,587.4119	7,587.4131	7,587.4147	7,587.4169
7,287.2592					7,287.2626
7,224.1121					7,224.1076
6,421.0270					6,421.0285
5,993.8495					
5,870.9183	5,870.9143	5,870.9164	5,870.9159	5,870.9149	5,870.9144
5,649.5650					5,649.5616
5,570.2899	5,570.2889	5,570.2894	5,570.2882	5,570.2892	5,570.2877
5,562.2259	5,562.2259	5,562.2257		5,562.2238	5,562.2255
4,550.2984	4,550.2975				
4,463.6903	4,463.6874	4,463.6898	4,463.6887	4,463.6875	
4,453.9203	4,453.9184	4,453.9193	4,453.9180	4,453.9176	
4,425.1913	4,425.1904	4,425.1927		4,425.1883	4,425.1909
4,418.7693	4,418.7684				
4,410.3682	4,410.3693				
4,399.9682	4,399.9672	4,399.9683	4,399.9648		
4,376.1222	4,376.1192	4,376.1219	4,376.1222		
4,362.6442	4,362.6422	4,362.6424	4,362.6446	4,362.6409	
4,351.3612	4,351.3602	4,351.3621		4,351.3584	4,351.3611
		4,319.5803	4,319.5802		
		4,318.5519	4,318.5495		
4,300.4882	4,300.4872	4,300.4888		4,300.4868	4,300.4875
4,286.4870	4,286.4861	4,286.4903		4,286.4858	4,286.4881
4,282.9680	4,282.9671	4,282.9698	4,282.9685	4,282.9669	
4,273.9700	4,273.9711	4,273.9705	4,273.9706	4,273.9681	

TABLE 6.—*Comparison of corrected xenon wave lengths*

5*c* 15 mm March 5 3 hours	10*b* 40 mm March 10 1 hour, 15 minutes	15*a* 15 mm May 20 2 hours	16*a* 25 mm May 21 2 hours	16*b* 25 mm May 21 1 hour	17 15 mm June 10 12 hours
	9, 162. 6512	9, 162. 6588	9, 162. 6495	9, 162. 6451	9, 162. 6525
	9, 045. 4429	9, 045. 4386	9, 045. 4443	9, 045. 4471	9, 045. 4446
	8, 952. 2533	8, 952. 2549	8, 952. 2529	8, 952. 2496	8, 952. 2533
8, 819. 4161	8, 819. 4106	8, 819. 4149	8, 819. 4165	8, 819. 4135	
8, 409. 1896	8, 409. 1904	8, 409. 1906	8, 409. 1887	8, 409. 1888	
8, 346. 8285	8, 346. 8248	8, 346. 8261	8, 346. 8223	8, 346. 8205	
		8, 280. 1175	8, 280. 1156	8, 280. 1160	
8, 231. 6342	8, 231. 6340	8, 231. 6375	8, 231. 6337	8, 231. 6352	
		7, 967. 3517.	7, 967. 3363		
		7, 887. 3899	7, 887. 3897		
7, 642. 0265	7, 642. 0220	7, 642. 0243	7, 642. 0237	7, 642. 0294	
		7, 584. 6836	7, 584. 6796	7, 584. 6785	
			7, 393. 7910		
			7, 386. 0023		
			7, 285. 2977		
	7, 119. 5985	7, 119. 5946	7, 119. 5975	7, 119. 5949	
		6, 882. 1540	6, 882. 1538	6, 882. 1553	
			6, 827. 3148		
			6, 318. 0622		
		5, 028. 2783	5, 028. 2784	5, 028. 2782	
4, 923. 1530	4, 923. 1515	4, 923. 1536	4, 923. 1510	4, 923. 1536	
4, 916. 5090	4, 916. 5077	4, 916. 5091	4, 916. 5068	4, 916. 5057	
4, 843. 2939	4, 843. 2941	4, 843. 2925	4, 843. 2911	4, 843. 2927	
4, 829. 7108	4, 829. 7085	8, 829. 7081	4, 829. 7095	4, 829. 7064	
4, 807. 0208	4, 807. 0192	4, 807. 0235	4, 807. 0188	4, 807. 0172	
4, 792. 6187		4, 792. 6202	4, 792. 6178	4, 792. 6194	
4, 734. 1567	4, 734. 1518	4, 734. 1523	4, 734. 1515	4, 734. 1506	
4, 697. 0236	4, 697. 0223	4, 697. 0208	4, 697. 0187	4, 697. 0194	
4, 690. 9726	4, 690. 9704	4, 690. 9702	4, 690. 9707	4, 690. 9711	
4, 671. 2286		4, 671. 2257	4, 671. 2249	4, 671. 2232	
4, 624. 2776		4, 624. 2733	4, 624. 2753	4, 624. 2773	
4, 611. 8885		4, 611. 8898	4, 611. 8898	4, 611. 8908	
4, 582. 7474	4, 582. 7491	4, 582. 7472	4, 582. 7468	4, 582. 7469	
4, 524. 6793	4, 524. 6818	4, 524. 6808	4, 524. 6799	4, 524. 6796	
		4, 500. 9751	4, 500. 9793	4, 500. 9766	
4, 385. 7692		4, 385. 7685	4, 385. 7690	4, 385. 7698	
4, 383. 9102		4, 383. 9105	4, 383. 9093	4, 383. 9090	
4, 203. 6960		4, 203. 6954	4, 203. 6947	4, 203. 6941	
4, 193. 5320		4, 193. 5289	4, 193. 5302	4, 193. 5297	
			4, 135. 1226		
4, 116. 1160		4, 116. 1137	4, 116. 1149	4, 116. 1149	
4, 109. 7120		4, 109. 7082	4, 109. 7095	4, 109. 7094	
		4, 078. 8204	4, 078. 8205	4, 078. 8209	
3, 967. 5466		3, 967. 5420	3, 967. 5414.	3, 967. 5405	
		3, 950. 9267	3, 950. 9251	3, 950. 9245	

Data on individual xenon measurements are presented in Table 6. Exposures 5*c* and 10*b* were made under conditions already described, the Xe lines appearing as impurity lines. A new pure Xe tube was used for the first time in exposure 15*a*. One hour of use intervened between exposures 15*a* and 16*a* in addition to unrecorded time for adjusting. Another new tube was used in exposure 17. Only three lines were measured on this plate, since most of the others were over exposed. These three measurements are probably the best we have for the lines indicated, since they lie very close to the weighted mean. Here again we find no systematic variations. The differences between individual observation are apparently due to the usual errors of observation. Lines of medium intensity, free from hyperfine structure, and, therefore, yielding sharper patterns show

better agreement in the wave lengths than those less favorable for measurement. If a pressure effect were exhibited by xenon a similar effect would be expected in the spectra of other rare atmospheric gases. In this connection an investigation of possible variation of neon wave lengths with pressure by Meggers and Burns [19] in 1922 should be recalled. They prepared a series of neon tubes with pressures ranging from 0.1 mm Hg to several cm, and compared the wave lengths of the radiation with the fundamental standard, care being taken to maintain the Cd tube under constant conditions. They observed no change in wave length as large as 1 part in 10,000,000, which was the probable error of the observations, and concluded that wave lengths from Cd or Ne sources are reproducible within the limits of precision attainable in wave-length comparisons.

In further support of their contention that xenon exhibits a pressure shift, McLennan and Quinlan have compared the infrared grating measurements of Merrill [20] with those of Meggers, deBruin, and Humphreys.[21] It should be remembered that these two sets of data were obtained with a grating giving a scale of 10.4 A per mm and that no claim of precision greater than about 1 part in 200,000 is made for these measurements. The recent measurements are probably more reliable than the earlier ones because longer-lived tubes, permitting longer exposures, were available, and a larger number of spectrograms were measured. Differences between the two sets of data represent errors of observation and can not be called upon to prove a pressure shift. We, therefore, find no evidence for pressure shift in any of the rare gases used at pressures not exceeding a few cm Hg, and are forced to the conclusion that the decrease in wave lengths reported by McLennan and Quinlan is explained by errors of observation.

It may be of interest to add that we have observed a change of wave length of the arc lines of Kr and Xe under the conditions employed to excite the spark spectrum and attribute the phenomenon to Stark effect. When the tubes are operated with condensed discharges and series spark gap many of the arc lines are noticeably diffuse and unsymmetrical with their centers of gravity displaced toward longer wave lengths. With uncondensed discharges of direct or alternating current, exciting only the spectrum characteristic of neutral atoms, such Stark effects are entirely absent, the lines are exceedingly sharp and perfectly reproducible.

WASHINGTON, July 3, 1930.

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[19] Meggers and Burns, B. S. Sci. Papers (S441), 18, p. 185; 1922.
[20] Merrill, B. S. Sci. Papers, 15 (S345), p. 251; 1919.
[21] Meggers, deBruin, and Humphreys, B. S. Jour. Research, 3, p. 731; 1929.